Sample preparation for X-ray fluorescence analysis VII. Liquid sample

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1. Introduction

We have discussed about the feature of X-ray fluorescence analysis (XRF) which is quick and non-destructive analysis of liquid, solid and powder sample in the previous issues. In this paper, analysis examples of liquid samples are shown. Careful attention is required for handling of liquid sample, because there are many kinds of liquids such as water solution, organic solvent, oil, etc., and each one has various kinds of properties such as acid, alkaline, etc. In this issue, analysis method for liquid samples by wavelength dispersive X-ray fluorescence analysis spectrometer (WDX) is discussed.

2. Common sample preparation of liquid sample in XRF analysis

Figure 1 shows overall preparation methods for liquid sample[1]. "Liquid method (direct measurement)" is used for analysis of liquid sample filled in sample cell covered with thin sample film directly. "Droplet method" (filter paper method) is used for analysis of dried droplet solution on special filter paper. There are some methods such that the trace metallic component in solution is concentrated with reagent, and solidifying method (not included in Fig. 1) where oil sample is solidified with solidification reagent then analyzed[2],[3]. This issue describes details of liquid method and droplet method.

3. Liquid method

Liquid method is the way of pouring sample in a liquid sample cell. Figure 2 shows schematic diagram of liquid sample cells. Rigaku supplies both types of cells for tube above and tube below WDX systems, and liquid method is applicable both type of WDX. Pouring liquid sample into the cell is easier for the tube below type than for the tube above type.

On the other hand, when light elements are analyzed, it is necessary to purge helium gas into sample chamber. Since X-rays are attenuated by sample film and helium gas in the X-ray path, elements heavier than Na are analyzed in ordinary case.

3.1. Liquid sample cell

Table 1 shows typical liquid sample cells. Besides the Table 1, sample cells of various sizes and shapes are available, and it is necessary to select appropriate sample cell based on equipment and analysis purpose.

3.2. Sample film

3.2.1. Type of sample films

Sample film is also called analysis window or sample protection film. Materials of the films are roughly polypropylene, polyester and polyimide. The films with different materials have different characteristics of mechanical strength, chemical resistance, durability against X-ray irradiation, transmission factor of X-ray, etc., therefore, it is required to select appropriate film according to matching with sample category and analysis purpose. For example, polypropylene film is suitable for acid or alkaline solution, and polyester film is suitable for lubrication oil or fuel oil, etc. Note that it is necessary to check the impurity of film beforehand. For example, polyester film contains more impurities

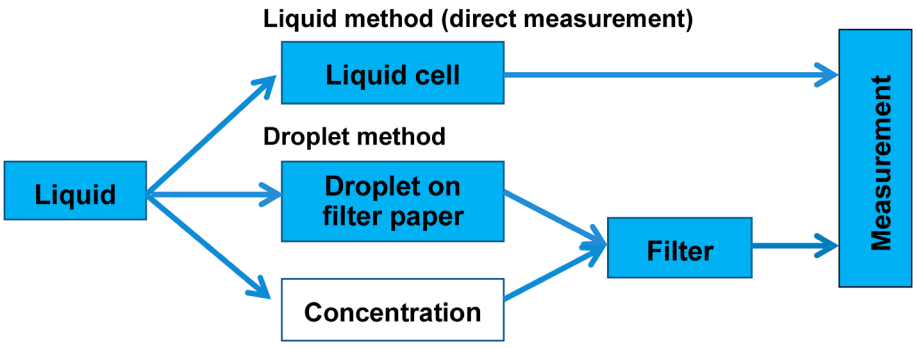


Fig. 1. Preparation methods for liquid sample.

* SBU WDX, X-ray Instrument Division, Rigaku Corporation.
** SBU EDX, X-ray Instrument Division, Rigaku Corporation.

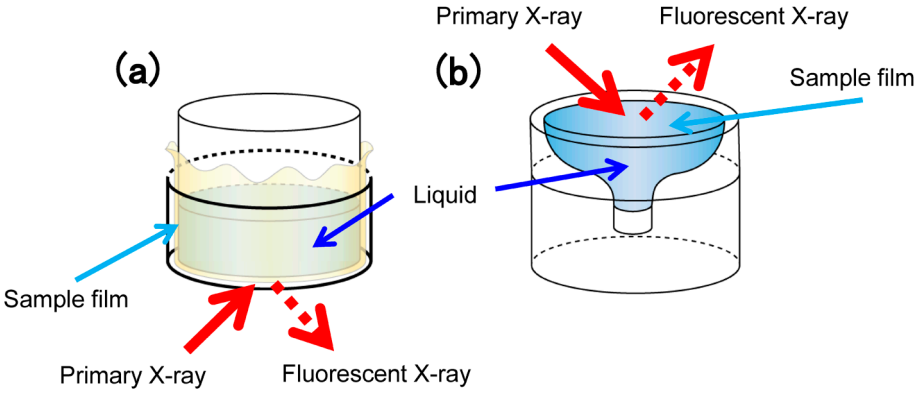


Fig. 2. Schematic diagram of liquid sample cells.
(a) For tube below type, (b) For tube above type.

Table 1. Typical sample cells for liquid and equipment used.

Cat. No.	CH1540	CH1340	CH1095	RS1240
Name	Sample cell for tube below (Double open type)	Sample cell for tube below (With lid)	Sample cell for tube below and scattering FP method	Sample cell for tube above (Single open type)
Inner diameter	31 mm	31 mm	38.1 mm	30 mm
Photo				
Equipment used with	ZSX Primus, Supermini200 etc.	ZSX Primus, Supermini200 etc.	ZSX Primus	ZSX Primus II ZSX Primus IV
Remarks	・For tube below type ・Film can be spread on both sides, and able to be sealed up.	・For tube below type ・Upside is a lid with ventilation hole, and easy to be assembled.	・For scattering FP method, and analysis surface is down side ・Sleeve type	・Analysis surface is upper side. ・Air bubbles do not remain on analysis surface as it is received in reservoir.

Table 2. List of polymer films used for sample film.

Name	Cat. No.	Thickness (μm)
Ultra-Polyester	CH 090	1.5
Mylar®	CH 100	2.5
Mylar®	CH 150	3.6
Prolene®	CH 416	4.0
Polypropylene	CH 425	6.0
Polyimide (Kapton®)	CH 440	7.5
Polypropylene	CH 475	12.0
Polypropylene	3399G003	6.0
Polyester	3399G001	6.0

Mylar : Registered trademark by Du Pont, USA
Prolene : Registered trademark by Chemplex, USA
Kapton : Registered trademark by Du Pont, USA

than polypropylene. Table 2 shows commonly used films. Roll type is less expensive and used widely, and the rectangular cut film or circular cut film is also available.

Generally, polypropylene film (thickness 6μm, Cat. No.3399G003) or polyester film (thickness 6μm, Cat. No.3399G001) are commonly used for high power WDX systems, and Prolene film (thickness 4μm, Cat. No.CH416) or Mylar film (thickness 3.6μm, Cat. No.CH150) for Supermini200.

3.2.2. X-ray transmission rate

Figure 3 shows transmission rate of common sample films. Long wavelength X-rays such as F-Kα do not transmit in most of the films. The stronger the film mechanical strength is, the smaller the transmission rate against long wavelength X-rays in general. From this fact, it is necessary that correction for the absorption by sample film is essential for semi-quantitative analysis (SQX analysis) with FP method.

3.2.3. Chemical resistance and durability against X-ray irradiation

Table 3 shows general chemical resistance and durability against X-ray irradiation of each film. It is obvious from the table that polypropylene is strong and

polyester is weak against acid and alkaline solution. As the chemical resistance is somewhat different from each solution, preliminary test using actual sample to confirm the duration must be executed. For checking the chemical resistance, it is recommended to put the sample into liquid sample cell with the film and to leave it for an hour or so, and then check whether swell or break of the film is observed or not. If it is observed, replacement of the film with any other type is to be considered.

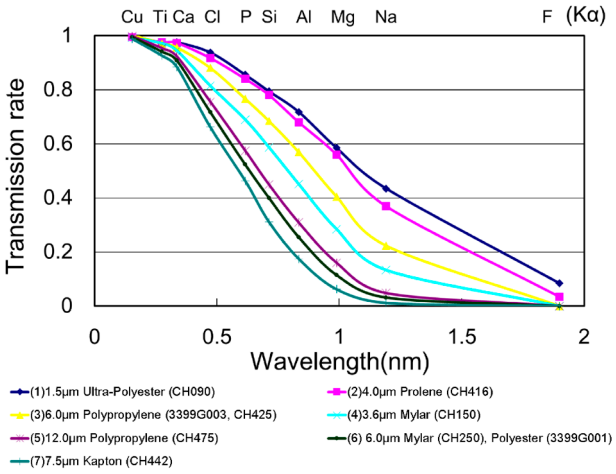


Fig. 3. X-ray transmission rate of each film.

Also, strong irradiation of primary X-rays causes deterioration of film. That is, mechanical strength of film is weakened by X-ray irradiation which breaks bonding among C, H and O. Durability of film against X-rays largely depends on material of film. Generally, polyimide has the strongest durability against X-rays followed by Mylar (polyester) and then polypropylene. In addition, the thinner film thickness is, the weaker durability against X-rays is. Bottom line of Table 3 shows the summary of the durability against X-rays. As the Prolene film has high transmission rate for X-ray and less impurity, it is easy to be handled. But, considering durability against X-rays, it is better not to use this film for the liquid sample analysis by high power WDX systems.

3.2.4. Impurity in the film

Generally, durability of the film against X-ray is correlated to the amount of additives such as Si, P, Ca and Al to enhance its characteristics. Care must be taken in case that these elements are analysis objects. Table 4 shows example of impurities contained in each film. These elements are detected as impurities originated from other material than the sample. It is possible to make correction for X-ray intensities of these elements originated from the film by executing impurity

Table 3. Chemical resistance and durability against X-ray irradiation of various films.

Chemical Classification	Type of film (t: Thickness)				
	Mylar (t: 6 μm)	Polypropylene (t: 6 μm)	Kapton (t: 7.5 μm)	Prolene (t: 4 μm)	Ultra-polyester (t: 1.5 μm)
Weak acids	○	◎	△	○	○
Strong acids	×	△	△	◎	×
Aliphatic, alcohols	◎	◎	○	◎	◎
Aldehydes	—	◎	◎	◎	—
Strong alkalis	×	◎	×	◎	×
Esters	×	○	○	○	×
Ethers	△	×	—	×	△
Aliphatic hydrocarbons	○	○	○	○	○
Aromatic hydrocarbons	△	△	△	△	△
Halogenated hydrocarbons	△	×	△	×	△
Ketones	◎	○	○	○	◎
Oxidizing agents	△	△	×	△	△
Durability against X-ray	○	○	◎	×	×(△)

◎: Excellent／○: Good／△: Fair／×: Not Recommended／—: Unknown

Table 4. Example of impurities in each film.

Film (Thickness)	Cat. No.	Mg	Al	Si	P	S	K	Ca	Mn
Polypropylene (6 μm)	3399G003	—	×	△	×	—	—	×	—
Polypropylene (12 μm)	CH475	—	×	△	×	△	—	△	—
Polyester (6 μm)	3399G001	△	—	◎	◎	—	—	○	—
Polyester (5 μm)	3399G002	—	◎	◎	○	×	△	×	○
Mylar (6 μm)	CH250	×	×	△	◎	×	—	◎	—
Kapton (7.5 μm)	CH250	—	—	△	◎	◎	—	—	—
Prolene (4 μm)	CH416	×	—	△	×	×	—	×	—

—: Not included at all ／×: Included extreme small amount ／△: Included small amount／○: Included ／◎: Included a lot

Table 5. Cause and provisions for film breakage.

Cause of film breakage	Provisions
Chemical resistance of sample film against analysis sample	Inspection of chemical resistance of sample film against analysis sample (Refer to 3.2.3)
Durability of sample film against X-ray	Lowering output of X-ray tube (kV-mA), Shortening measurement time, Use of primary beam filter, Use of thick sample film
Damage to sample film by activation of solution by X-ray irradiation	

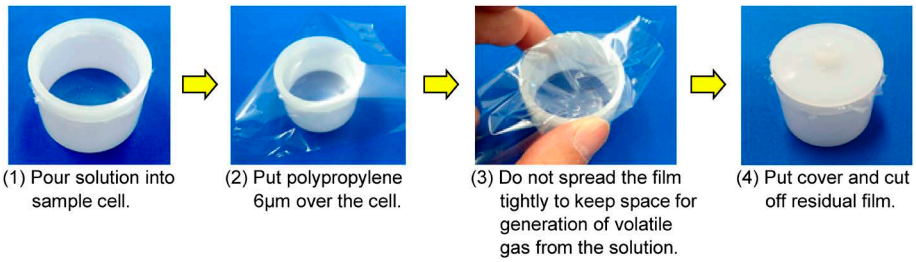


Fig. 4. Example of sample preparation steps for solution sample containing volatile gas.

correction in SQX analysis. As the amount of additives are different from lot to lot, it is important to check impurities using blank sample for every lot.

3.3. Precaution for the liquid method

3.3.1. Breakage of the film

Most important precaution for analysis by liquid method is scattering of liquid sample inside the spectrometer. Scattered solution caused by breakage of the film can result in serious damage to the system and cause system breakdown. Table 5 shows causes of film breakage and its provisions. Other than the Table 5, as knowledge of the sample solution will be very important information, full attention is required for the analysis of totally unknown sample.

Quantitative analysis of liquid glass is a typical example of film breakage caused by chemical reaction. When polypropylene film is used for sample film as liquid glass is an alkaline solution, hardening of the film takes place by irradiation of X-rays and sample film sometimes breaks in a short analysis time. It is necessary to lower the tube current and shorten X-ray irradiation time as much as possible to cope with it as shown in Table 5. It is also effective to prepare multiple samples and analyze one element per one sample as all example. Besides, organic solvent requires deep attention to the compatibility with film.

3.3.2. Precaution for setting measuring conditions

Longer total measurement time increases the risk of sample problems. To reduce measurement time, increasing scan speed for qualitative analysis, utilizing fixed angle analysis and cutting down number of analysis elements are effective. For example, measurement of Na when 6μm Mylar film is used can be eliminated since transmission rate of 6μm Mylar for Na-Kα is almost zero. Safe measurement times varies depending on film type. For polypropylene (6μm) measurement time should be within 10 minutes, within 15 minutes for Mylar (6μm) and within 20 minutes for Kapton (7.5μm). Moreover, it is also effective to use primary beam filter as a measuring condition. Especially the primary beam filter is effective for tube below type equipment.

3.3.3. Other precaution

Once acid solution sample is scattered in the system, it causes serious damage to the system. To avoid it, as mentioned before, it is important to minimize damage to the film and sample by X-rays and heat by taking measures such as setting short measurement times (within 10 minutes), lowering output power (kV-mA) of X-ray tube, employment of primary beam filter, etc. Thick polypropylene film is useful for strong acid.

Analysis of strong acid samples or samples containing high levels of F, S, Cl, etc. must be performed carefully as they may be volatile generating gas causing damage to the system and sample cross-contamination. Sealing up solution sample as shown in Fig. 4 can prevent such problems. It is recommended to shorten the analysis time by half compared to ordinary samples for highly volatile samples such as light oil, gasoline, etc. as the heat causes additional volatilization in the cell resulting in expansion of film on analysis surface. Even for sealed samples, it is desired to shorten measurement time as much as possible since some components slightly pass through the film and scatters in the equipment. It is also recommended that samples are quickly removed from sample holder after measurement.

Moreover, in the case of samples containing components which precipitates after leaving unattended for a long time such as dispersion medium, it is recommended to measure after removal of precipitating substance as much as possible. It is necessary for oil samples to take provisions such as shortening measurement time or the like as dissolved component might sometimes be precipitated by irradiation of X-rays.

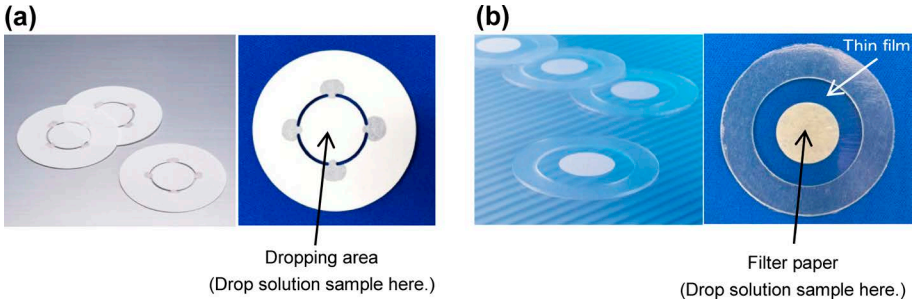


Fig. 5. (a) MicroCarry, (b) UltraCarry.

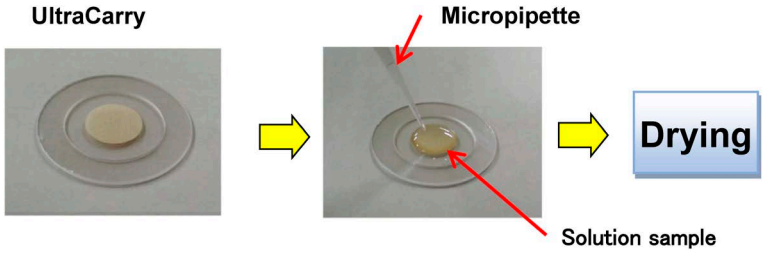


Fig. 6. Sample preparation method for filter paper.

Sample cell is basically expected to be disposable. When it is reused after cleansing, it is necessary to pay attention to contamination by the components in the sample of previous measurement.

4. Droplet method

Droplet method is the way to measure a filter paper, etc. on which liquid sample is dropped and then dried. It makes possible to measure light elements such as B, F, Na, Mg, etc. in liquid sample with high sensitivity because measurement can be carried out under vacuum atmosphere and without sample film. Although any filter paper available on the market can be used, highly accurate analysis is possible with special filter paper (MicroCarry) which has a slit to prevent expansion of sample solution. It is designed for XRF use, and a specific sample solution amount is pipetted on it. Besides, high sensitivity filters (UltraCarry, UltraCarry Light) having dropping area which gives much higher sensitivity for water solution type samples are also available.

4.1. Outline of MicroCarry and UltraCarry

Analysis of ultra-trace element in solution with high sensitivity is possible by using MicroCarry and UltraCarry (Refer to Fig. 5). Both of them are analyzable by dropping solution sample directly on it and drying. Moreover, the UltraCarry makes analysis of several 10 ppb level possible by making sample solution concentrated previously. Droplet method is mainly applicable to the analysis of water solution sample, but it may sometimes not have good reproducibility for solution samples with low surface tension such as surface active agents or organic solvents because of spreading of solution to outside dropping area.

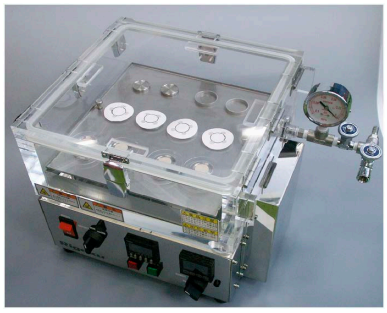


Fig. 7. Sample vacuum oven (UltraDry).

4.2. UltraCarry, UltraCarry Light

The UltraCarry is an accessory of a special filter paper for collection of elements on an extremely thin film[4]. Thinner filter paper compared with general filter paper is employed to reduce background which improves lower detection limit. Moreover, it has a feature to hold up to 500 μL. The UltraCarry Light has less light element impurities (especially Ca, K, S, P, Si, Mg) compared to UltraCarry. Use of the UltraCarry Light is recommended in case analysis of light element is needed.

4.3. Sample preparation for droplet method

Sample preparation method for the MicroCarry and the UltraCarry is discussed in this chapter. First, place the filter paper on a suitable plate. For the MicroCarry, since solution penetrates into MicroCarry, dropping area of filter paper must not come in contact with the plate. Next, take a certain amount of sample solution into a micropipette and pipette onto the filter paper. Droplet amount is set to 50−100 μL for the MicroCarry, and to 500 μL for the UltraCarry. Dry up the solution quickly at constant temperature between 40−60°C keeping dust

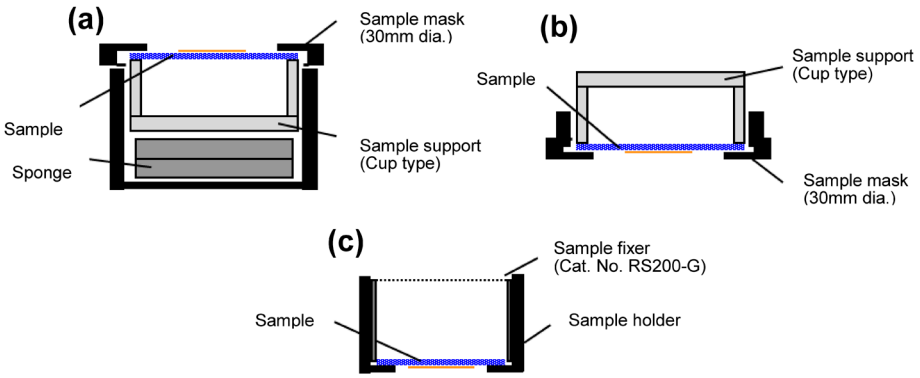


Fig. 8. Sample setting of filter paper.
(a) For high power tube above type WDX (ZSX Primus II, ZSX Primus III+, ZSX Primus IV, etc.)
(b) For high power tube below type WDX (ZSX Primus),
(c) For benchtop tube below type WDX (Supermini200, etc.)

or the like out. In the case of the MicroCarry, drying at 60°C or higher will risk melting of wax that prevents expansion of sample solution and warping of filter paper. In the case of the UltraCarry, high temperature might peel the filter paper off the film. Figure 6 shows sample preparation method for the UltraCarry. It is same for the MicroCarry.

In the case of high density solution that creates crystal deposition, crystal deposition of sample may be observed on the filter paper after drying. In this case it is recommended to dilute the sample solution since crystal deposition causes large analysis error.

Regarding the way of drying of these filter papers, natural drying is accepted, but it takes several hours. Figure 7 shows the sample vacuum oven (UltraDry) which is designed for drying filter paper and makes possible to dry it quickly. Different from general vacuum oven, the UltraDry is equipped with a heat source nearby to prevent freezing of solution due to decompression such that efficient drying of solution has become possible.

4.4. Precaution for droplet method

In droplet method, sample after preparation can be handled much easier than liquid method as it is in a dry form. However, precaution for measurement time is to be considered well as it is possible to be broken after being irradiated by X-rays for a long time.

Since the filter paper is so thin that X-rays is transmitted easily, impurity X-rays originated from sample holder or sample support can be detected. A way of sample setting is shown in Fig. 8. In the case of analysis by high power WDX, use of sample cup (cup type sample support) is effective for reducing impurity X-rays from sample support as much as possible. In case of Supermini200, use of sample fixer for analysis of filter paper (Cat. No. RS200-G) is effective to reduce scattering X-rays from sample holder.

Characteristic X-rays from elements contained in the filter itself are also detected as impurity X-rays in the same way as sample film. In this case, impurity X-rays correction after conducting qualitative analysis of blank filter beforehand and registration of X-ray intensity is necessary.

5. Summary

Sample preparation of liquid sample for liquid method and droplet method are discussed in this issue. Although both methods are simple for analysis, it is necessary to make sample preparation carefully to prevent leakage and scattering of liquid, especially for liquid method. It is important to set up suitable conditions for analysis purpose by carrying out prior examination of compatibility between film and sample, possibility of generation of gas, etc. in advance.

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